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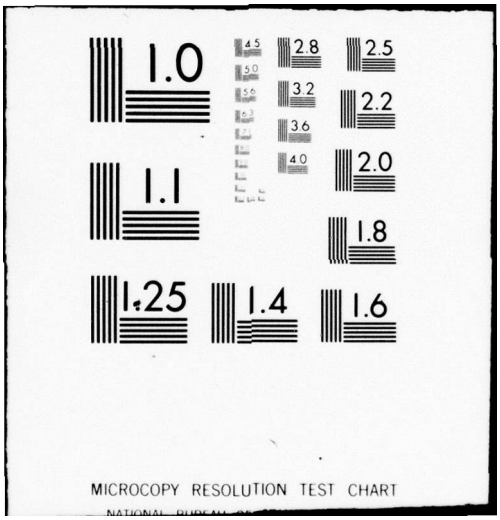
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IMPROVEMENT OF GaAs CRYSTAL QUALITY BY MEANS OF LIQUID-SOLID INTERFACE CURVATURE CONTROL

Final Scientific Report

June 1, 1977 through May 31, 1978
Contract F49620-77-C-0105

Prepared for
Directorate of Electronic and Solid State Sciences
Air Force Office of Scientific Research
Bolling Air Force Base, DC 20332

by

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Schenectady, NY 12301

August 1978

SRD-78-112

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This report serves to document the experimental difficulties and the various steps taken in this vertical freezing technique.

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This report serves to document the experimental difficulties and the various steps taken in this vertical freezing technique.

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LIST OF ILLUSTRATIONS (CONT'D)

FOREWORD

This program is intended to investigate the effect of the liquid-solid interface curvature on the crystal quality of GaAs grown from the melt in the vertical freezing technique. The work was carried out in the Solid State Communications Branch, Signal Electronics Laboratory, General Electric Corporate Research and Development, Schenectady, NY. The work is sponsored by the Department of The Air Force, Air Force Office of Scientific Research, Bolling Air Force Base, DC 20332, under Contract No. F49620-77-C-0105 (June 1, 1977 through May 31, 1978) which is an extension of Contract No. F49620-76-C-0127 (June 1, 1976 through May 31, 1977). The present Final Report not only is a continuation of the Interim Report which covers the first year's work, but also includes a condensed version of the Interim report for completeness.

At the General Electric Company, the work was carried out under the supervision of Dr. David W. Oliver, Acting Manager of the Solid State Communications Branch. The principal investigator is Dr. W. Tantraporn, assisted by Mr. Jacob C. Bortscheller.

The Air Force Program Manager prior to December 1, 1977, was Dr. W.R. Steinbach, AFOSR. Program management has been transferred to Dr. D.H. Reynolds, AFAL, since that date.

IMPROVEMENT OF GaAs CRYSTAL QUALITY BY MEANS OF LIQUID-SOLID INTERFACE CURVATURE CONTROL

I. INTRODUCTION

At the meeting of a group of GaAs specialists organized by Professor H. Gatos of the Massachusetts Institute of Technology in November 1977, it was generally agreed that although work on GaAs has been in progress for at least 25 years, the growth of GaAs single crystals still remains an irreproducible and erratic art. Present commercial sources strive to provide GaAs wafers of larger sizes with more uniform characteristics. The quality of the crystals as judged from the performance of the devices fabricated from the crystals still varies. Because of their relatively low cost when compared with device fabrication costs, the crystals are merely "screened" via various means and only those judged acceptable are used in device production. This wasteful practice will suffice as long as the quantity demand remains low.

Anticipating the need for better quality GaAs substrates in larger quantity in the future, AFOSR has been interested in supporting an investigation of an alternate means of producing GaAs single crystals. The prevailing method used for GaAs growth by the commercial sources is the horizontal Bridgman gradient-freeze technique. In general, although not always, the "quality" of the crystal is best near the seed and deteriorates toward the other end. The crystals are also Ga-rich; sometimes Ga droplets can be observed in the wafer when viewed through an infrared microscope. The Czochralski technique, known to produce very high quality GaAs on occasion, is not suitable for commercial production because of the size limitation and generally higher production cost.

Unlike the Czochalski setup, where appropriate thermal shields can be placed to control the liquid-solid interface curvature, the horizontal Bridgman gradient freeze technique does not lend itself to easy control of the interface curvature. Richard[1] studied the effect of the liquid-solid interface curvature on GaAs growth using the horizontal zone melting technique; the short zone produces a dipole-like heat flow so that the isothermal contour is not planar. He reported that the best quality obtains when the interface is very slightly solid-convex, while the solid-concave interface is definitely very bad. Chang et al.[2,3] were successful in demonstrating the virtue of the solid-convex interface in the case of naphthalene and concluded: "We see no reason why large diameter useful GaAs cannot be produced by this technique ..."[3] even though their GaAs experiment was not successful.

It was felt that while the commercial GaAs crystal suppliers continued to improve on the horizontal Bridgman technique with some government support (for example, see Reference 4), the effect of interface curvature along the line suggested by Chang et al.[3] deserved further investigation. The latter was proposed despite Weisberg's[5] statement that "the compounds expand upon freezing

and therefore are badly strained when constrained by crucibles. Therefore, the vertical Bridgman (1925) or Stockbarger (1936) technique is not suitable."

The general approach taken was that the experiment should be set up first in the simplest form. The problems were to be observed from experiment and means to alleviate these problems were to be provided along the way. The first-year work involved construction of the vertically moved zone melting furnace and simple sample container. The result at the end of the first year was encouraging. The second-year work, however, uncovered additional problems which are now believed to be inherent, and very likely will remain unsolved. Termination of the program is recommended.

The arrangement of this report is as follows. The program goals and original approach are discussed in Section II. Since the nature of the work is exploratory and experimental, the approach has been continuously modified to accommodate new findings and therefore is discussed under experiments and results (Section III) in essentially chronological order. The conclusion and recommendations are given in Section IV. References are listed in Section V. Several experimental results such as the temperature profile measurements and miscellaneous techniques are given in the Appendices in order to allow continuity of the crystal-growth discussion.

II. PROGRAM GOALS AND ORIGINAL APPROACH

The general objective of this program is to establish a means of obtaining large/long GaAs single crystals of high quality.

The proposed approach is to study the effect on the crystal quality of the solid-liquid interface curvature during growth of GaAs from the melt, in the belief that an appropriate curvature can be found and experimental procedures can be established to yield the desired crystal.

The original experimental approach to carrying out the study objective was to use the vertical zone melting technique. The thermal configuration would be similar to a "short dipole" field like the one shown in Figure 1. It can be seen that with the addition of a constant background temperature the melting point isothermal contour can be selected to be solid concave, planar, or solid convex, by simply adjusting the background temperature.

The vertical quartz tube containing the GaAs charge is tapered at the lower end. The hot zone passes the tip from below. Without controlled seeding, the very small volume at the tip first solidified would serve as the seed and presumably single crystal growth should result.

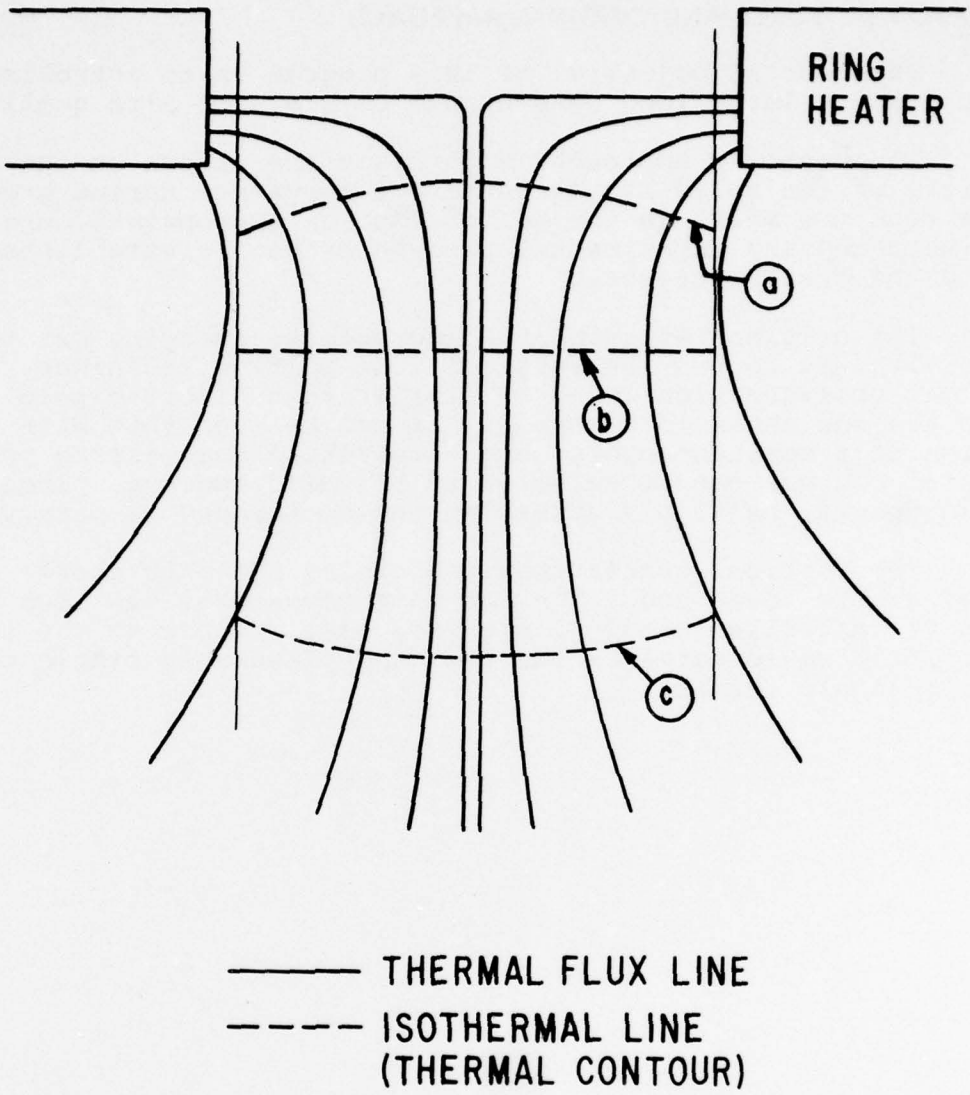

Figure 1. Qualitative illustration of a "short dipole-like" thermal configuration. With the melt near the ring heater and the crystallized portion below, the melting temperature contour can be (a) solid convex, (b) planar, or (c) solid concave, depending on the background temperature superposed on the nonuniform distribution.

III. EXPERIMENTS AND RESULTS

A. SUMMARY OF THE FIRST YEAR'S WORK

The proposed experimental program for the first year consisted of the following steps:

1. Design and construction of a vertical movement to support the existing, calibrated furnace so that the growth rate could be selected and controlled.
2. Design and construction of a sample holder to monitor and minimize vibrations.
3. Recalibration of the temperature profile (cylindrical coordinates r,z).
4. Regrowth runs using polycrystalline GaAs in a sealed evacuated quartz tube tapered to a point at the lower end (to provide an arbitrarily oriented seed) under various temperature and growth speed conditions.
5. Evaluation of the crystal quality by x-rays and etch-pit density counting.
6. Establishment of the best growth conditions and production of high-quality GaAs crystals.

Step 1 of the experimental program was successfully completed. The calibrated movement provides a constant speed of from 0.35 mm/h to 32 mm/h over a vertical distance of 12 inches with vertical "play" limited to less than 20 mils (Figure 2).

Step 2 was also successfully completed. A series of experiments resulted in the choice of a simple air-cushion, three-leg, shock mounting. A vibration monitor capable of recording the logarithmic amplitude of sample vibrations at frequencies from 0 to 15 kHz was built. The mechanical vibrations of the sample holder were reduced by shock mounting to a level limited by noises in the air. (See also Appendix A.)

In Step 3, experiments were performed and the temperature profile of the furnace was established. (See Appendix B.)

Step 4 consisted of a number of experiments. Crystal regrowth was carried out twice according to the scheme proposed originally. Poor results were obtained from the first run as the result of a less-than-optimal cold-zone temperature used to regulate the As pressure. The second run resulted in an explosion during the hot-zone downward movement. The short liquid zone was followed by a solidifying GaAs plug that closed off the equilibrium transport of As to the cold zone and resulted in a high-pressure buildup in the melt.

The furnace vertical temperature profile was then modified to insure that initially the GaAs would be liquid over the entire

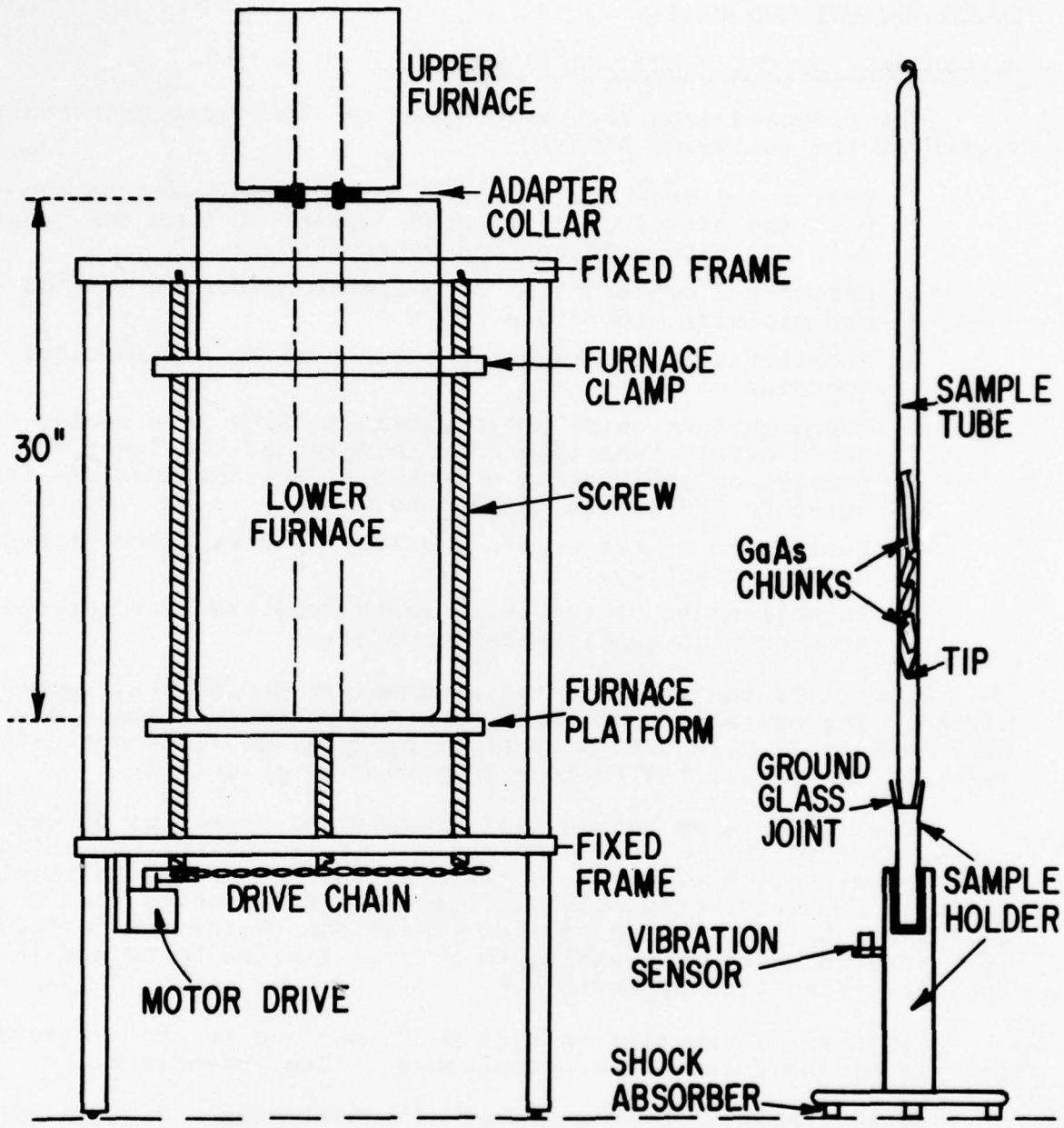

Figure 2. Schematic diagram of the furnace movement and the sample mounting. The furnace platform and furnace clamp are simultaneously moved by three screw rods at a controlled rate. The lower furnace is controlled by two controllers. A third controller controls the temperature near the adapter collar for As pressure regulation by energizing the upper furnace. The sample is inserted into the furnace from the top into the sample holder. Vertical alignment of the furnace core and the sample is critical with the small clearance required to minimize convection effects.

sample length. The temperature contour curvature at the lower end of the furnace was found to be less than that at the corresponding position with the short-dipole-like configuration, but still appreciable. (See also Appendix B.)

The third and fourth regrowth runs were made with the new furnace profile. Vertical variations existed in the resulting ingot which were visible as bands of various shades of silver and gray (Figure 3). The silvery coating starting at the tip was identified as excess As precipitating out during crystallization. This indicated that the temperature of the melt was not constant despite temperature control to better than $\pm$0.5 C at the thermocouple position.

The thermocouple had been located at a position where the melting temperature contour was expected; thus control could be exerted at the crystallizing interface. However, this position allows the melt temperature to have a wide range, depending on the temperature gradients across the melting point isothermal surface. These temperature gradients, in turn, depend on thermal conductivity nonuniformities. During the period before, during, and after the sample tip is in the controlled zone, the controlled zone comprises air, air plus the sample cone, and the sample rod, respectively. Thus the temperature above the controlled zone can vary widely during the growth procedure.

The thermal conductivity nonuniformities not only affect the z-direction thermal profile discussed above but also produce adverse profile curvature. This is illustrated in Figure 4. Here a uniform one-dimensional heat flow is shown perturbed by the presence of the higher conductivity sample tip. The flat temperature profile in air at the interface, T_i, becomes solid-concave in the conical section of the sample. Because the thermal conductivity disparity between GaAs and air is appreciable, the solid-convex type of temperature contour originally present in the air-core furnace can be overcome by the presence of the sample cone, and a solid-concave type contour results. It is believed that this did occur in our experiment and prevented us from attaining Step 6 of the first year objective.

Step 5 of the experimental program proposed originally was carried out to the extent required with the samples available. X-ray diffraction measurements were made to check the size of the crystals in the polycrystalline regrowth ingot of Run 3 and showed that the ingot consists of a few large single crystals. The polycrystallinity of the regrown ingot is attributed to multiple seedings caused by the improper T_i contour. Etch-pit counting has not been carried out; the crystals obtained so far have been obviously poor. Auger electron analysis was performed to identify the surface layer's composition in the various "bands" mentioned earlier.

At the end of the first year, the furnace was rewound with new, all Pt windings. They replaced the burned-out section of the furnace originally designed to be the lower temperature portion

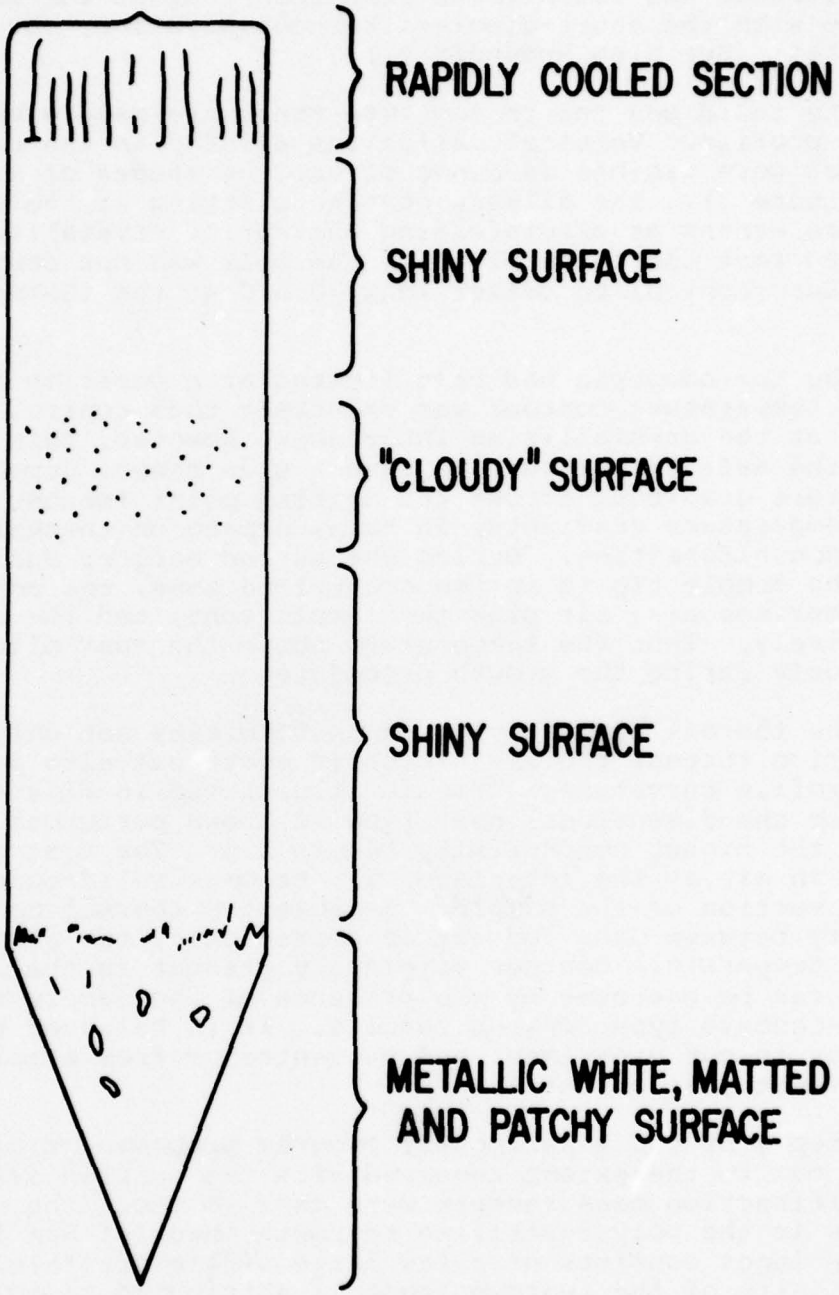

Figure 3. Sketch of GaAs ingot obtained from Run 3. This ingot, obtained at the end of the first year's work, indicates the different melt temperatures during the movement of the sample out of the hot zone caused by changing thermal profile.

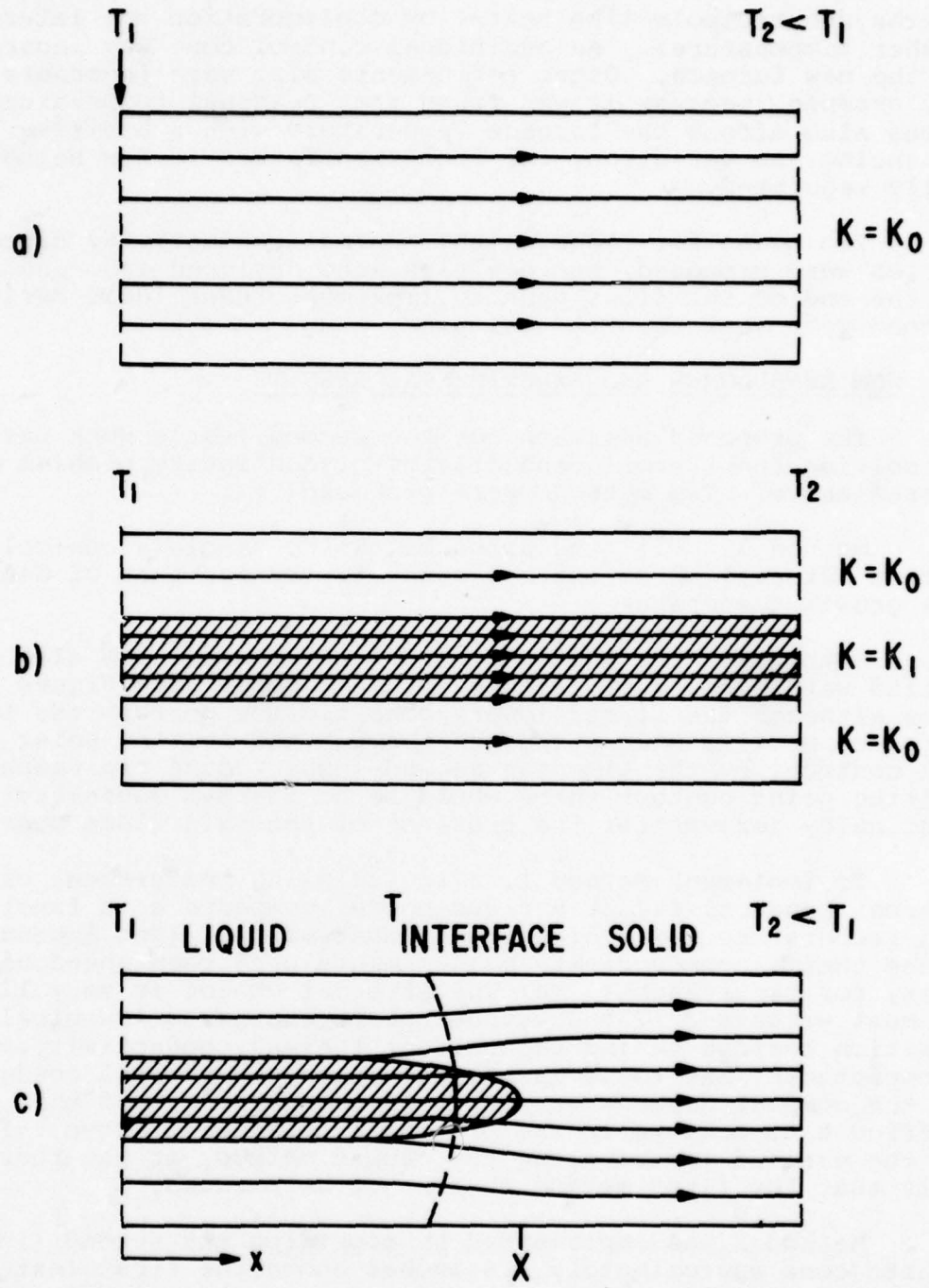

Figure 4. Qualitative description of thermal flux lines under three conditions.
(a) Uniform flow, air core.
(b) When part of the core is more conductive uniformly over the whole length.
(c) When part of the core is more conductive only over a portion of the length, the isothermal contour becomes curved.

in the short-dipole-like heat-flow configuration but later used at higher temperatures. An additional control zone was incorporated in the new furnace. Other refinements also were incorporated. For example, because it was found that seasonal temperature variations also affect the furnace temperature with a positive feedback enhancing the variation, the room temperature is now being carefully regulated.

Two means for reducing the thermal conductivity discontinuities were proposed, and new rigs were designed and constructed at the end of the first year to implement these ideas during the second year work reported below.

B. NEW APPROACHES AND EXPERIMENTAL RESULTS

The proposed approach for the second year's work was aimed at solving the thermal conductivity discontinuity problem discussed above. Two methods were proposed:

Method 1. Fill the space below the sample's conical tip with a material whose thermal conductivity is $\gtrsim$ that of GaAs at the growth temperature.

Method 2. Let the space below the conical tip also be filled with GaAs, i.e., a cone within a cone. See Figure 5. Thus although the first (lower) cone tip may perturb the temperature profile when it passes through the melting point isothermal contour, by the time the second (upper) cone tip reaches the melting point contour there would be no thermal conductivity discontinuity (except for the presence of the thin glass cone).

To implement Method 1, a rig allowing measurement of the thermal conductivity of various powder compacts as a function of the temperature was designed and constructed. (See Appendix C.) These thermal conductivity measurements were soon abandoned, however, for two reasons: (a) The material choice is very limited; it must withstand 1250 C without phase changes or chemical decomposition besides having the correct thermal conductivity. (b) The "compactness" has to be maintained since the thermal conductivity of the compact depends very much on the packing, and this is very difficult to achieve in the present experimental setup. In view of the ease of implementing the second method, it was therefore felt that the first method should not be pursued.

Method 2 was implemented by providing the second (internal) quartz cone approximately 2.5 inches above the first (external) cone. The liquid zone length before crystallization is approximately 7 inches (See Appendix B), so above 5 inches of ingot length above the second cone is the subject of interest.

Again, similar to the first year's objective, the second year's work was to study the crystal quality as a function of the solid-liquid interface curvature. The latter can be varied by slightly increasing or decreasing the average temperature. (See Section II.)

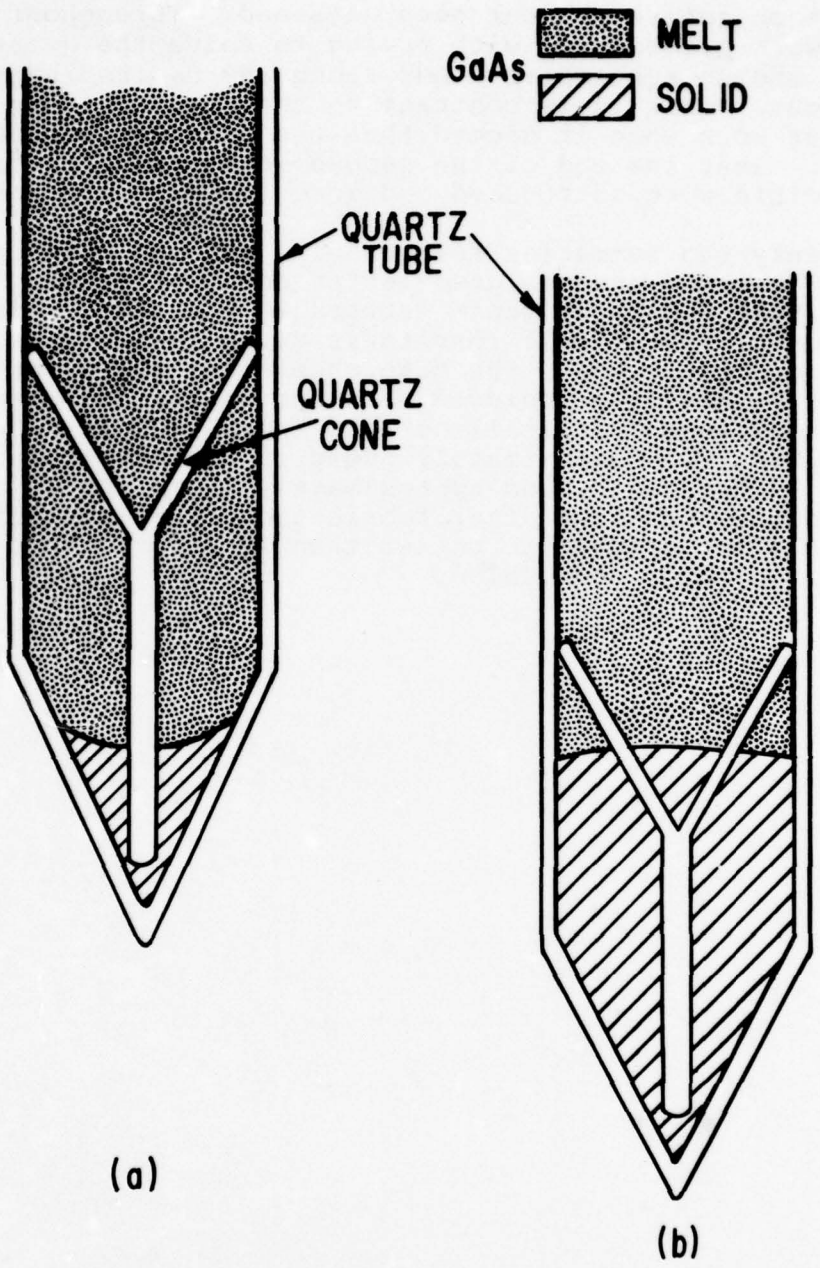

Figure 5. Double-cone approach to reducing thermal conductivity discontinuity effect. As in Figure 4, the melting point isothermal contour is solid concave when the sample tip leaves the melt region (a). In (b) when sufficient length of the sample has passed the melting point isothermal contour the latter can resume the shape intended in the furnace design, for example, the solid convex contour in Figure 1.

The objective has not been attained. Throughout the second year we were preoccupied with trying to solve the quartz breakage problem, and no systematic study along any desired path could be carried out. This is in contrast to the result of Run 3 of the first year work when it seemed that the breakage problem was not critical. Near the end of the second year graphite coating and a BN crucible were introduced and some improvements were noted.

Twenty run summaries follow. The various container types used are depicted and assigned letter designations in Figure 6. They are referred to by these letters in the summary data sheets. Discussion of the overall results is given in Section III C. For the sake of completeness the data sheets for the first year (Runs 1 through 4) are also included. Except where otherwise noted the raw material is polycrystalline GaAs (purchased from Crystal Specialties, Inc.). Approximately 500 g is used for each run to produce the 7-inch ingot, and approximately 1 g of As is added. The quartz tube is annealed after fabrication, H_2-fired before loading, evacuated after loading to better than 10^{-7} torr via a well-trapped Hg-diffusion pump, and sealed.

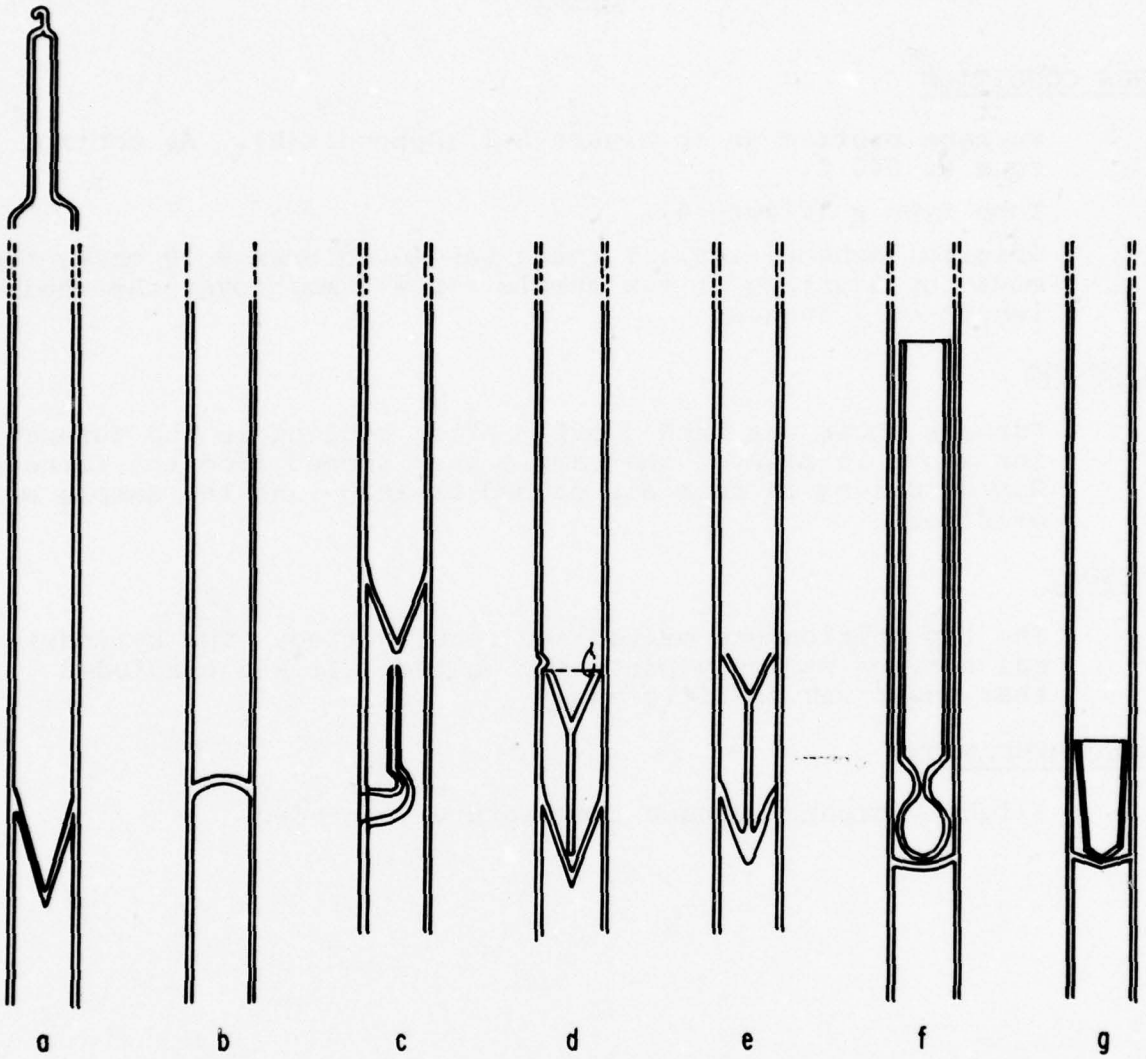

Figure 6. Various quartz container configurations used in the GaAs regrowth experiment.
(a) Initial design.
(b) Test design expecting bad result.
(c) A design allowing cooling of the tip by N_2 flow.
(d) Double-cone design. Three depressions on the side wall are to hold the inside cone.
(e) Double cone design with attached stem.
(f) Necking down growth selection. Outside tube is to prevent oxidation in the event of breakage of the inner tube.
(g) BN crucible. Outside tube for As pressure containment only.

RUN 1

RUN CONDITION

Furnace profile as in Figure A-1 (Appendix B). As control zone at 640 C.

Tube type a (Figure 6).

Original scheme, i.e., furnace was moved down @ 30 mm/h, then moved up starting at the sample tip @ 7 mm/h over the whole length of 7 inches.

COOLING

Furnace power was turned off. After cooling in the furnace for about 15 minutes the sample was removed from the furnace. Rapid cooling in room air caused breakage and the sample was oxidized.

RESULT

The tip portion was melted and resolidified. The cylindrical portion was only partially melted. It was concluded that power was insufficient.

RECOMMENDATION

Slightly higher furnace temperature is needed.

RUN 2

RUN CONDITION

Same as Run 1, but with As control zone at 650 C. This should raise the overall furnace temperature in the region between the molten zone and the As control zone.

RESULT

Explosion occurred during the melting-down cycle.

HYPOTHESIS

As soon as the molten zone is moved down there was a solid plug of GaAs above the molten zone cutting off communication with the As control zone. The vapor pressure of the hot zone caused the tube to explode.

RECOMMENDATION

The sample should be melted over the entire length then solidified from the tip end.

RUN 3

RUN CONDITION

Same tube type as Run 1, i.e., type a.

New furnace profile, Figure A-4 (Appendix B).

Total length molten, solidified from lower end @ 3.5 mm/h.

COOLING

Furnace power off and sample allowed to cool in the furnace down to room temperature.

RESULT

The sample was intact, but external appearance (See Figure 3) suggested that the melt temperature varied during passage of the melting point temperature contour from below. Polycrystalline results (few large grains).

HYPOTHESIS

Since there was only one sampling/control thermocouple at 5 3/4 inch position of the furnace, the temperatures at higher inch positions can vary.

RECOMMENDATION

Add another sampling/control thermocouple at 12-inch position to control the melt temperature.

RUN 4

RUN CONDITION

Tube type b. Bad result is expected. The run was made to make sure that the solid convex interface, built in at the start, might, in fact, show some surprising results.

Same furnace condition as Run 3. The recommended change from Run 3 had not been carried out.

Growth speed ≈6 mm/hr.

COOLING

Power slowly decreased in the bottom coil while the rest of the furnace power remained on, in order to "gradient freeze" the portion of the sample at the upper end if it had not solidified already.

RESULT

The tube cracked below the low end, probably because of poor glass work. The crack propagated up. The sample was oxidized.

The ingot is polycrystalline.

RECOMMENDATION

No further work on this tube type.

RUN 5

RUN CONDITION

Same as Run No. 3

Recommended furnace change had not been implemented.

Growth speed 2.5 mm/h.

COOLING

Lowest portion of the furnace slowly cooled while other portions remained as set for the following 1 1/2 hours; then all furnace power was turned off.

RESULT

The top 3/4 inch showed a quick-freeze characteristic, so the slow-cool gradient freezing was not slow enough.

The tube cracked at the cone-joint, and devitrified over the ingot length.

The sample was slightly oxidized and was polycrystalline.

RECOMMENDATION

The proposed change in furnace control must be implemented before further test runs are made.

RUN 6

RUN CONDITION

Tube type d (See Figure 6).

Furnace profile as in Figure A-4 with additional controller controlling the temperature at the 12-inch position.

As pressure control temperature 625 C.

RESULT

Top furnace burned out during power up. As pressure → 0, causing fractionation of the GaAs. Sample was lost.

RUN 7

RUN CONDITION

Same as Run 6; the top furnace had been repaired. Growth speed 3.4 mm/h.

COOLING

Bottom furnace slowly cooled: 2 mV over 5 hours, then off. The As controlling top furnace remained on 8 minutes after the lower furnace was turned off.

RESULT

Tube cracked during cooling. Severe devitrification. The cracks seemed to have originated from the dimples (holding the inside cone, type d tube).

The sample has a "quick freeze" zone at the top end. It is polycrystalline even above the inside cone, with mostly vertical grain boundaries. The interface was slightly oxidized. The white oxide was x-ray analyzed to be Ga_2O_3.

RECOMMENDATION

The growth tube was too long and the As control portion too narrow. Slight design change is called for.

RUN 8

RUN CONDITION

Same furnace profile as Run 7.

Tube type c (Figure 6). Slight cooling of the sample tip is provided for by 5 cc/min N_2 flow. Convergence of thermal flex lines toward the tip should promote the solid-convex growth condition. Growth speed is 3.4 mm/h.

COOLING

All furnace power off at the end of the movement; sample allowed to cool in the furnace.

RESULT

The tube cracked in the region 3/4 inch to 2 1/4 inch (measured from the tip) and showed devitrification over ingot length.

Beside the "quick freeze" zone at the very top the surface texture of the ingot showed 3 bands of finish. The ingot is polycrystalline with mostly vertical grain boundaries. The quantity of As collected on the top part of the tube is larger than the As chunk put in.

RECOMMENDATION

Increase the As control temperature from 625 to 630 C.

RUN 9

RUN CONDITION

Repetition of Run 7, except that instead of being shock mounted the sample is mounted on a 60-rpm rotating platform. Growth speed is 3.4 mm/h.

COOLING

Bottom furnace off, followed after 12 min by the middle furnace off, and followed after 1 1/2 hours by the top furnace off.

RESULT

Ingot was polycrystalline and Ga-rich. The tube cracked during the run but was still mechanically intact.

RECOMMENDATION

Check the top furnace controller; As loss should not have occurred.

RUN 10

RUN CONDITION

Tube type e (Figure 6).

Furnace condition similar to Run 8. Arsenic control zone was recalibrated and set at 630 C.

Growth speed 3 mm/h.

COOLING

All furnace power off. Allowed to cool in the furnace.

RESULT

Tube cracked during the run near the outside cone attachment; the sample was oxidized. Seeding from the inner cone was not successful; the ingot was polycrystalline. The sample did not appear to be Ga-rich.

RECOMMENDATION

New construction of the outside cone. Try flaring the cone so that the attachment surface is more nearly perpendicular to the cylinder wall.

RUN 11

RUN CONDITION

Type e, as in Run 10, but the outside cone attachment was "improved." Same furnace temperature profile as in Run 10, except the bottom portion set at slightly lower temperature (by 0.1 mV)

Growth speed is 3.5 mm/h.

COOLING

Low and middle furnace off, then top furnace off ≈10 min later.

RESULT

High degree of devitrification. Tube cracked during the run again near the outside cone attachment, and the sample was oxidized.

RUN 12

RUN CONDITION

Attempt to synthesize GaAs from Ga and As.

201.18 g of Ga and 216.22 g of As were put in an inner tube and the latter was placed in the type f growth tube (Figure 6).

RESULT

Explosion occurred about 2 hours after furnace startup.

Apparently the As control zone has insufficient volume to hold the As before saturation, and the As solid-vapor interface was therefore forced to move to a higher temperature. The explosion ruined the furnace.

RECOMMENDATION

Must use GaAs charge unless the tube is modified.

RUN 13

RUN CONDITION

Tube type f, filled with 355.16 g GaAs, and about 0.5 As. Same furnace profile as Run 10 but with repaired furnace. Growth speed ≈3 mm/h.

COOLING

Bottom furnace was cooled at 0.5 mV/10 min, then all power off.

RESULT

The outside tube did not crack. Because there was an opening between the outside and inside tube, when the tip was passed much below the melting point temperature contour it became a cold trap for As. Sample was polycrystalline and Ga-rich.

RUN 14

RUN CONDITION

The tube was of type f, but instead of the inner tube, a carbon cloth (Union Carbide WCA graphite cloth 1/16 inch thick) was used to line the inside of the tube to prevent GaAs wetting of quartz.

Mid-furnace control (12-inch position thermocouple) was set 0.7 mV higher than the bottom furnace control (5 3/4 inch position thermocouple).

Gradient freeze cooling technique for growth.

COOLING

Both thermocouples were simultaneously slowly voltage-compensated at the same rate, 0.7 mV in 48 hours, then at a gradually faster rate to reach room temperature in 16 hours.

RESULT

Tube did not crack despite severe devitrification. Middle coil of the furnace burned out during cooling; the As control zone moved down and became independent of the top furnace. As condensation occurred. Sample decomposed and was Ga-rich.

RUN 15

RUN CONDITION

Another attempt to synthesize from 231.98 g of Ga and 254.68 g of As. Tube was type a, with pyrolytic graphite coating to about 9 inches above the cone tip. Tube's upper end was of larger diameter, cf. Run 12.

Very slow increase in the furnace temperature to allow for As absorption into Ga.

RESULT

Explosion occurred after 6 hours of slow temperature increase; the temperature at the bottom furnace was less than 1000 C.

RECOMMENDATION

No further attempt is to be made in the vertical tube configuration to synthesize GaAs from the components. The dissolution of As in Ga is too slow.

RUN 16

RUN CONDITION

116 g of GaAs and 0.55 g As were loaded into BN crucible of tube type g (Figure 6). The top of the tube was modified to accept a thermocouple which sampled the temperature at the center of the collar section between the two furnaces. This thermocouple is then used to control the As pressure, set at 625 C.

Furnace was rewound and recalibrated to have the same temperature profile as before (Figure A-4).

Growth rate 3.6 mm/h by furnace movement.

COOLING

"Gradient freeze" cooling rate as in Run 15.

RESULT

Mid-furnace coil burned out near the end of the cooling cycle. Tube was severely devitrified and cracked near the top, probably after the mid-furnace burned out.

Ingot was polycrystalline. Shiny surface implied no wetting to BN.

RUN 17

RUN CONDITION

Ingot from Run 16 was reused.

10 g of new GaAs and ≈0.5 cc of As were added.

Same tube type g with new BN crucible.

COOLING

Gradient freeze cooling as in Runs 15 and 16, but shortened the first period to 20 hours instead of 48 hours.

RESULT

Ingot was polycrystalline and Ga-rich. The reason for the latter result is not understood, for the thermal settings were the same as for Run 16.

RUN 18

RUN CONDITION

Only 420.13 g of GaAs and ≈ 0.5 cc of As were loaded in the tube type g except no Bn crucible was used. The inside of the tube was pyrolytic-graphite coated to ≈ 8 inches above the tip.

Furnace profile set similar to that for Run 16.

Growth speed 3.3 mm/h by furnace movement.

COOLING

Use the "gradient freeze" cooling ramp for 14 hours.

RESULT

Tube was severely devitrified and broke above the ingot. The ingot was polycrystalline and showed a short quick-freeze zone at the upper end. It was Ga-rich.

Pyrolytic graphite seemed to have left the lower part of the tube in favor of the colder top. Apparently it did not prevent GaAs-quartz wetting.

RUN 19

RUN CONDITION

121.93 g of GaAs and 15.92 g As were loaded in the Bn crucible, which in turn was floated on 250 g of Ga liquid in the tube type g. The inside of the tube was previously coated with pyrolytic graphite. Same furnace settings as Run 16.

RESULT

The tube collapsed inward during the furnace movement @ ≈3.5 mm/h. Apparently the Ga liquid absorbed As. The GaAs in the BN decomposed. It was hoped that there would be sufficient As above the Ga and that the opening between the BN crucible and the inside wall is sufficiently narrow so that the As absorption would be slow enough to last through the run. This was not the case.

RUN 20

RUN CONDITION

385.37 g GaAs, 2.80 g As and ≈2 cc of B_2O_3 were put in the tube type a which had been pyrolytic graphite coated earlier.

Furnace settings as in Run No. 16.

Growth rate ≈4 mm/h by furnace movement.

COOLING

"Gradient freeze" rampers used over 39 hours.

RESULT

Tube cracked a little near the cone attachment but not all the way through. Pyrolytic graphite seemed to have smoked up the wall and redeposited as soots in the upper section. Thin "spiral tape" of As was deposited along the upper part of the tube. Tip of the cone was filled with B_2O_3 but has sharp hole near center. GaAs did not wet the B_2O_3 hole.

Side surface of ingot had B_2O_3 powder attached.

Ingot was >90% single crystal. Small region of polycrystalline along one side.

RECOMMENDATION

B_2O_3 seemed to allow single crystal seeding. If effort is to be continued, perhaps B_2O_3 coating inside the tube would help solve the glass strain and wetting problem.

C. DISCUSSION OF EXPERIMENTAL RESULTS

As seen in the summary data sheets above most of the runs did not yield ingots for study; the quartz tube broke and the material was oxidized. Those few runs which were carried out to completion without breakage yielded polycrystalline ingots. Below we discuss the quartz breakage problem and the crystal quality of the ingots. The poor crystal quality and the breakage problem will be seen to have a common cause.

1. Quartz Breakage

Although some breakage or even explosion did occur during the heat-up cycle (for example, in Run 12 where the raw materials Ga and As were used instead of the already synthesized GaAs), most breakages occurred after an appreciable portion of the recrystallized ingot had traversed below the melting point temperature zone. In general severe devitrification of the quartz was observed, sometimes to the point of "snow-flaking" characterized by white chips falling off the tube almost continuously. Devitrification also was observed as initiated in the colder, lower zone and propagated toward the hotter zone at the same speed as the furnace movement, so that there was a distinct boundary of devitrification at a given time. Complete passing of the sample downward then resulted in completing the devitrification region over the entire ingot length. (Devitrification of quartz is known to be more severe at higher temperature and higher humidity. It is more severe during the summer months.)

Because of the explosion during Run 12, the furnace was rewound. The core of the available ceramic tube size was slightly larger. In the vertical furnace there is always unavoidable air convection current even with the top end of the furnace tube closed to minimize the "chimney" effect. The convection was believed to be more troublesome in the new furnace core; more severe devitrification was observed, presumably due to easier access of room moisture into the furnace.

The very fact that this is a vertical furnace configuration is believed to be largely responsible for most of the critical problems which prevent attainment of the objective of the curvature effect study. Such study in the horizontal configuration has been successfully demonstrated[1]. In the horizontal system the liquid does not fill the cross section of the tube and the solid remains in contact with the vapor phase. In the vertical configuration the grown solid portion is in contact with the liquid phase only. It was initially hoped that the problem of non-stoichiometry could be better controlled in the vertical configuration, and since the non-stoichiometric problem is believed to be very important the vertical configuration was pursued despite the Weisberg statement[5].

The desire to have isothermal interface of controlled curvature also necessitates a thermal configuration with very large

thermal gradients. See Figure 1. The change in curvature from solid-convex to concave is within small distances, implying large axial as well as radial temperature gradients. Theoretically the curvature needed for good growth can be less. In order that the isothermal surface curvature can be measured, however, large gradients were built in. As shown in Appendix B, even with large gradients the accuracy of the data is still rather poor; small differences in large signals must be obtained.

Such large thermal gradients are believed to be responsible for initiating microcracks leading to devitrification and quartz breakage slightly below the molten temperature zone, i.e., at the maximum gradient position. (See the temperature profile in Appendix B.) Here the solidified GaAs carries the heat from the hot zone while the quartz is cooled by the surrounding air. As a result,(1) the inner wall of the quartz is hotter than the outside and (2) the GaAs is still very hot and has not contracted to the same degree as the quartz despite a larger thermal coefficient. Therefore, the sample usually cracks when a sufficient length of GaAs reaches into the non-radiant region of the furnace. (When the total sample is cool the GaAs is actually loose in the tube, having contracted more.)

Ironically, the large temperature gradients built into the system in order to study the thermal profile curvature effect itself are responsible for preventing attainment of the objective. The vertical Bridgman configuration is at the mercy of the convection outside the tube pumping in more moisture which leads to more quartz devitrification and a shift of the thermal profiles.

2. Crystal Quality

The normal method of grading the crystal quality involves cutting and polishing an x-ray oriented $\{111\}_A$ surface and etching it to reveal the etch pits. These processes are time-consuming and costly. The crystals obtained from the recrystallization runs so far have been obviously bad and the processing costs are not justified.

It turns out that when the GaAs ingot is cut by a fine-diamond wheel, the abrasions on the surface are different for different crystallographic orientations, so that crystal grains are vividly revealed in room light as patches of different shades of gray. See for example Figure 7. The polycrystallinity and grain size are therefore easily documented.

The proposed "seeding from a point" using the cone implies wetting of the quartz by the GaAs liquid; otherwise the liquid would not reach into the tip. Seeding from the tip is therefore self-defeating in that the wetting also causes continuous seeding from the surface. Even within a very small volume near the tip a very large number of small polycrystalline grains are obtained. In some rare cases one grain becomes dominant and occupies a relatively large volume of the subsequently grown ingot.

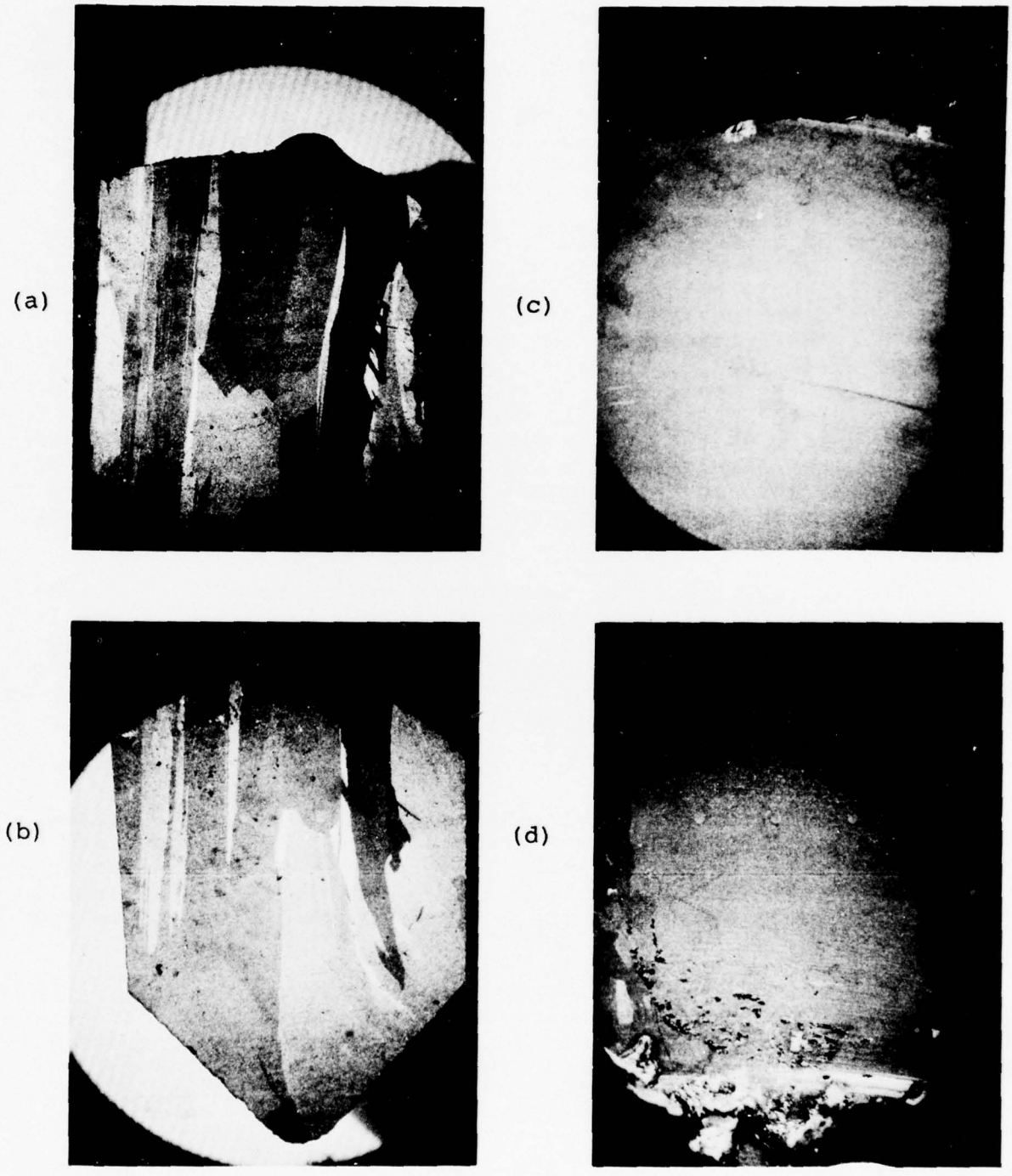

Figure 7. Photograph of the ingots from Runs 16 and 20. Each ingot was cut lengthwise by a diamond wheel. The surface texture clearly shows the different crystal grains of various sizes. Photographs (a) and (b) show top and bottom sections of ingot from Run 16; (c) and (d) show top and bottom sections of ingot from Run 20. In (c) some water marks may be visible. The line looking like a crack is actually a saw blade mark (a slip by the operator). In (d) side grains and voids are visible.

The expansion-upon-solidification effect of GaAs manifests itself as separation (breakage) of the solid in the cone tip region. As a new layer solidifies, it seeks a larger diameter space and therefore moves up the cone forming horizontal bands (discs) of solid in the small section of the cone, especially when the cone angle is more sharply tapered.

Seeding from the cone tip therefore was not successful. Attempts were made to prevent the GaAs wall-wetting by using a carbon-cloth lining (Run 14) and pyrolytic graphite coating (Runs 18-20). The carbon-cloth approach introduced a more severe problem: the solid communicated with the vapor, and because of the temperature gradient the GaAs decomposed.

The graphite coating appeared smooth and hole-free before the sample was heated in the recrystallization furnace. Afterwards this smooth coating of the lower section disappeared and carbon deposits were found instead in the upper, cooler section of the tube. The carbon coating failed to prevent wetting.

In fact, it is the carbon soot pattern in the tube that suggests a strong convection current of air in the annular space between the quartz tube and the furnace wall. Because neither the furnace core tube nor the quartz sample tube is perfectly straight, the space between them does not have a uniform annular cross section and the air convection current "snakes" through a path of minimum flow-resistance. The carbon soot traces the path as a spiral; we are not certain whether the pattern is positive or negative of the thermal pattern caused by the convection.

A boron-nitride crucible was also used as the inner container within the quartz tubing (Runs 16, 17, and 19). Although the GaAs did not wet BN, the strain relieving effect, if any, was insufficient and the ingots were all polycrystalline.

The use of B_2O_3 in Run 20 yielded the most interesting result (see Figure 7).[3] Although the ingot is Ga-rich and has a rough external surface, it is 90% single crystal. If means could be found to coat the inside of the growth tube with B_2O_3 and if such coating could be maintained during crystal growth, a single crystal would very likely be obtained with the type a tube. However, it is unlikely that the effect of the interface profile curvature could be studied, for the thermal profile still would always change depending on the relative position of the ingot in the furnace.

IV. CONCLUSIONS AND RECOMMENDATIONS

When a high quality single crystal GaAs is obtained from the Czochralski system, one of the experimental conditions is that the growing surface of the solid must be horizontal or convex.[6] The planar or slightly solid-convex interface is also required for good growth in the horizontal Bridgman experiment.[1] But here the solid convexity must be very small; larger convexity causes other kinds of defects.

As the solid grows, equilibrium conditions among the 3 phases (solid, liquid, and vapor) must be maintained in order to have uniformity in the solid. This implies very small thermal gradients in the horizontal Bridgman technique, where the three phases freely interact. Note that the curvature in an isothermal surface implies existence of radial as well as axial thermal gradients. Hence, requirements for larger curvature and small gradients are mutually exclusive. The horizontal Bridgman technique cannot take advantage of a larger solid-convexity. In the liquid-encapsulated Czochralski technique, interaction between the grown solid and the vapor is reduced and one can make use of the solid convexity growth condition to a larger degree. In addition, the generally increasing crystal cross section in the Czochralski technique is already more conducive to the solid-convexity without larger temperature gradients compared with those required in a constant cross section case.

In a vertical Bridgman system such as ours the growth tube is radially filled and the vapor-solid communication is excluded. In principle this should allow a larger range of study of the effect of the solid-convexity on the crystal quality. However, the stress caused by the GaAs expansion upon solidification within the tube is so great that good single crystals cannot be obtained, as predicted by Weisberg.[5] Furthermore, the thermal conductivity difference between the quartz container and the GaAs tends to cause quartz breakage as discussed above. The breakage tendency is aggravated by the temperature gradients required to produce the solid-convex thermal profile. In rare cases when quartz breakage was successfully avoided, the ingots obtained were polycrystalline.

Since good solid-convexity at the growth interface and the good strain free condition in the grown solid are mutually exclusive, and since a suitable "soft container" and access to seeding cannot be found in the vertical Bridgman technique, it is recommended that further curvature effect study be terminated.

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Appendix A

Shock-Mounting and Vibration Monitoring

In order to determine the validity of the shock-mounting, first a sensitive vibration monitoring circuit was built. A sensitive accelerometer (BBN, model 507) with 100 mV/g sensitivity and 15 kHz bandwidth is attached to the sample holder. The signal from its preamplifier is further amplified up to a factor of 10^3. A peak-reading amplifier and a logarithmic converter are then used, and the converted signal is fed to the strip chart recorder. At the maximum sensitivity the vibration monitor can record vibrations caused by normal speaking voices within 30 feet. The general noises (air and floor vibration, plus electrical) comprise about 10% of full scale at the highest sensitivity.

With this monitor, it was found that "foam-rubber and weights" type of cushioning was very poor for reducing the vibrations on the sample holder. The best result was obtained with a simple 3-point support of the sample holder platform by the air shock-absorber motor mounts (Barry Mount, 770 6G). These mounts not only are excellent shock absorbers, reducing the amplitude of test vibrations to within the general noise level, but also allow easy plumbing of the sample holder's vertical alignment. The latter can be achieved by simply shifting a weight around on the platform.

Appendix B

Furnace Temperature Profiles

The original furnace temperature profile along the Z (vertical) direction is shown in Figure A-1 and the radial temperature distribution is shown in Figure A-2. The profile measurement was carried out by moving the thermocouple within the furnace core. There were no baffles within the core to reduce the convection, although the upper end of the furnace was closed. The profile was used for crystal regrowth runs 1 and 2. A set of isothermal contours is presented in Figure A-3.

The temperature profile of the furnace for crystal regrowth runs after that is of the type shown in Figure A-4, with the radial distribution as shown in Figure A-5. Since the temperature settings were slightly changed from run to run, it is not practical to measure and present every thermal profile. Profiles were recalibrated after every furnace-burnout. This vertical profile measurement was carried out with the thermocouple centered in the core by a guide. The latter was in turn held in place by many discs which also served as convection-reducing baffles. The radial thermal distribution was measured by a gang of thermocouples rigidly fixed in a holder to the same height Z, at fixed radial distances. In the case of Figure A-5 the furnace core is essentially filled with powder alumina. For a qualitative understanding of the effect of the core-filling material, Figure A-6 shows the vertical temperature profile for three materials: SiC powder, alumina powder, and air for the same furnace power settings. One would assume from the result that in the case of GaAs solid, the higher thermal conductivity would bring the melting point isothermal contour to a lower inch-position, and also that the isothermal contour curvature would be smaller.

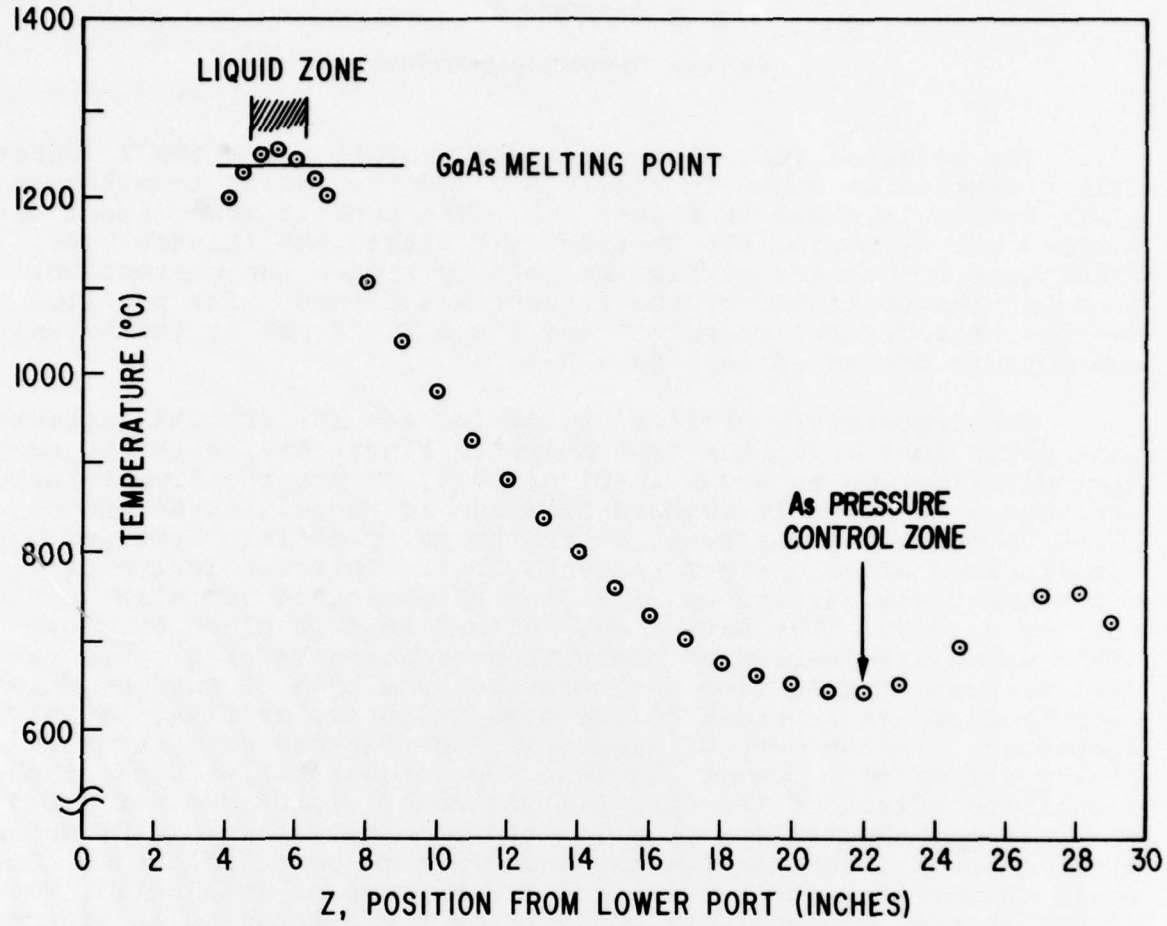

Figure A-1. The temperature profile as a function of height Z in the original furnace. The two-zone-controlled profile provides a short liquid zone (T > 1238 C) and a low temperature zone ≈650 C for controlling the As pressure.

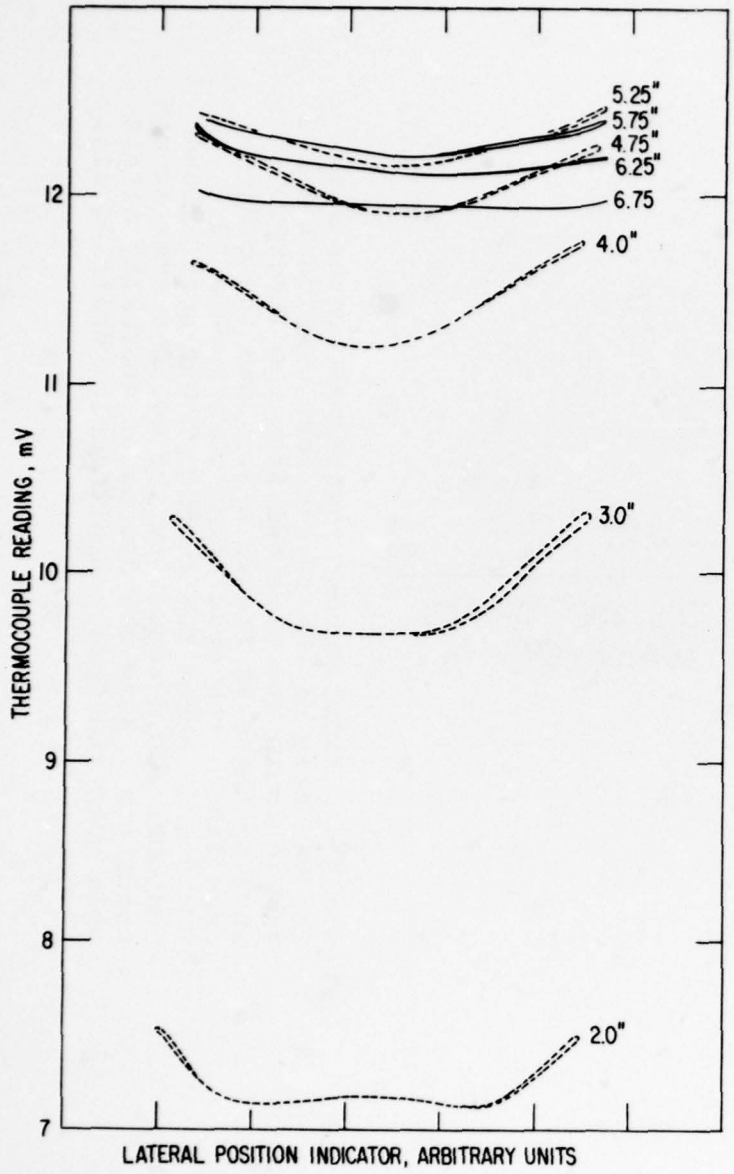

Figure A-2. Reproduction of the x-y recorder trace of the radial temperature distribution. The thermocouple reading is traced against the position-indicating voltage of a motorized mechanical scanner. The numbers on the curves indicate the thermocouple height position measured from the lower furnace port. Because the thermocouple clamp is not very rigid the height adjustment also introduces some sway in the lateral position indicator. The lateral span corresponds to 1.25". For the sake of clarity, many other traces are not shown. Note the intercepts, say, of the 4.75" and the 6.75" curves at 11.95 mV, indicating that the 11.95 mV isothermal contour must be curved to include the 4.75" and 6.75" heights. Many such intercepts on the same mV level constitute a single isothermal contour.

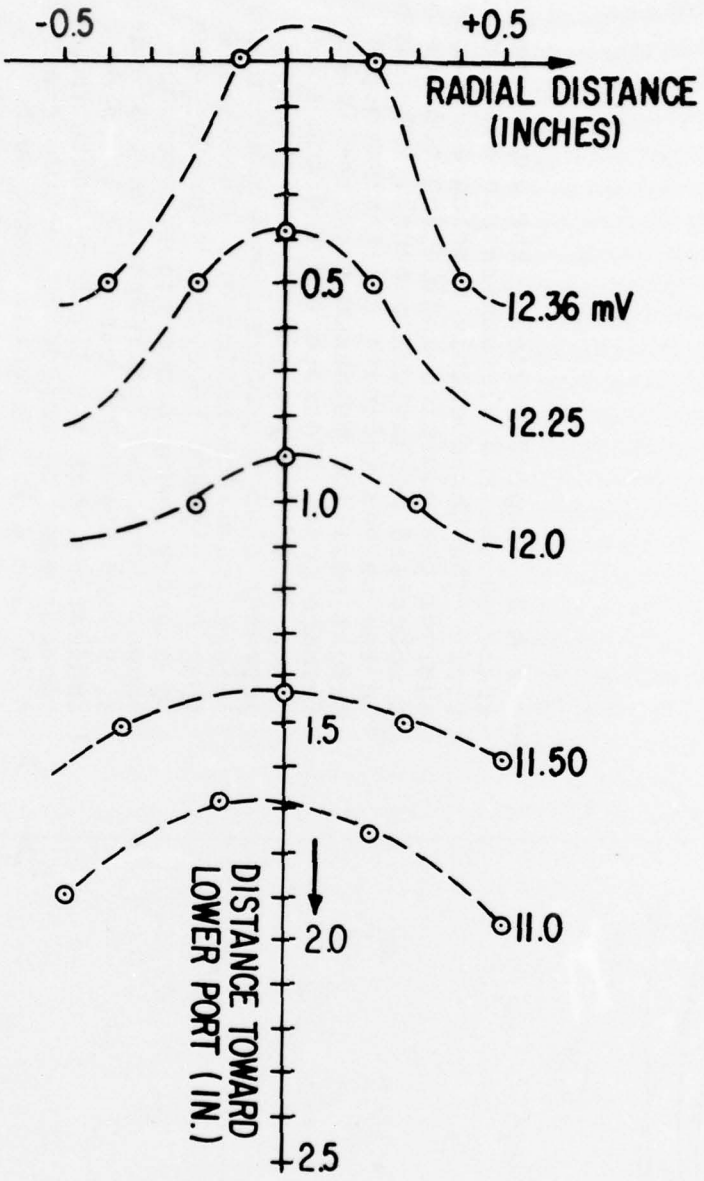

Figure A-3. Experimental isothermal contours in the vicinity of the molten zone of Figure A-1. The contours are obtained from the intercepts such as those in Figure A-2. Note the ordinate label; the zero point corresponds to Z = 5 3/8" above the furnace lower port. These contours would result in the solid-convex growth condition. Note the degree of convexity attainable when the core contains only unbaffled air.

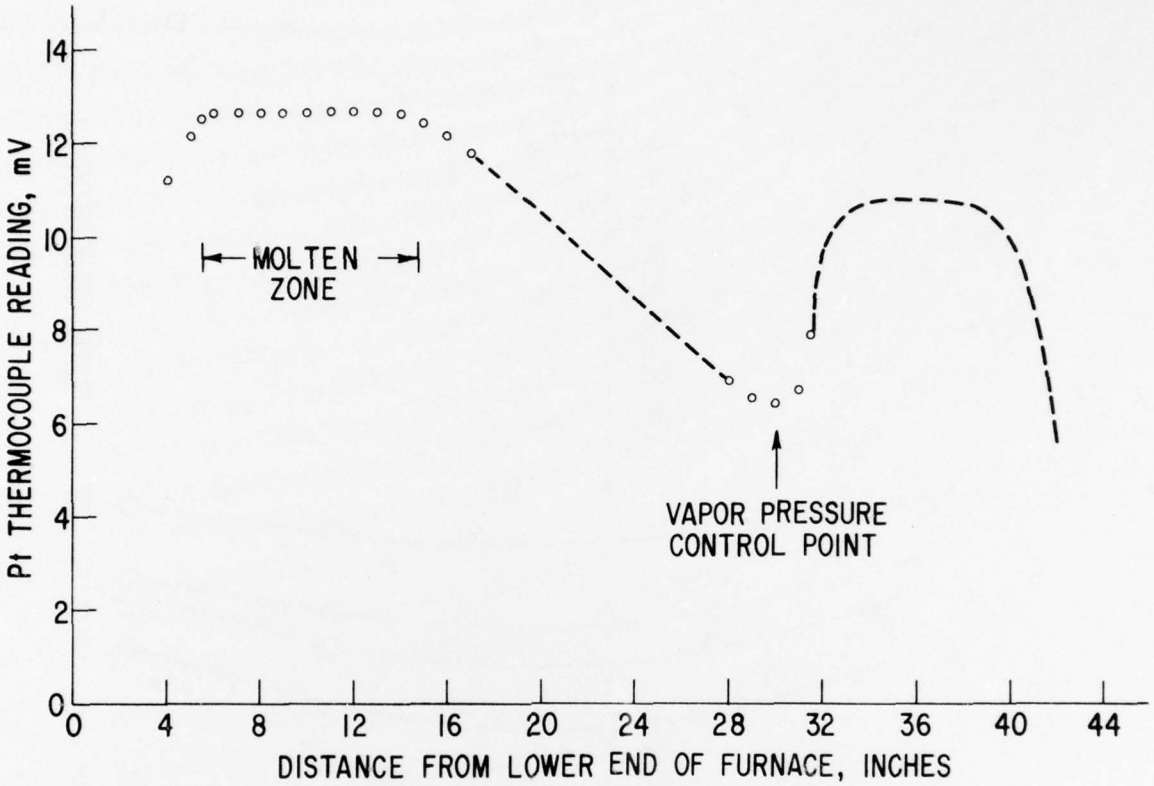

Figure A-4. New furnace profile to provide approximately 7 inches of GaAs molten zone. The section beyond the 30-inch position is actually an auxiliary furnace on top of the original furnace, and is primarily responsible for the As vapor pressure control. Cf. Figure A-1. Controller thermocouples are located at 5 3/4", 12", and 30 1/2" positions.

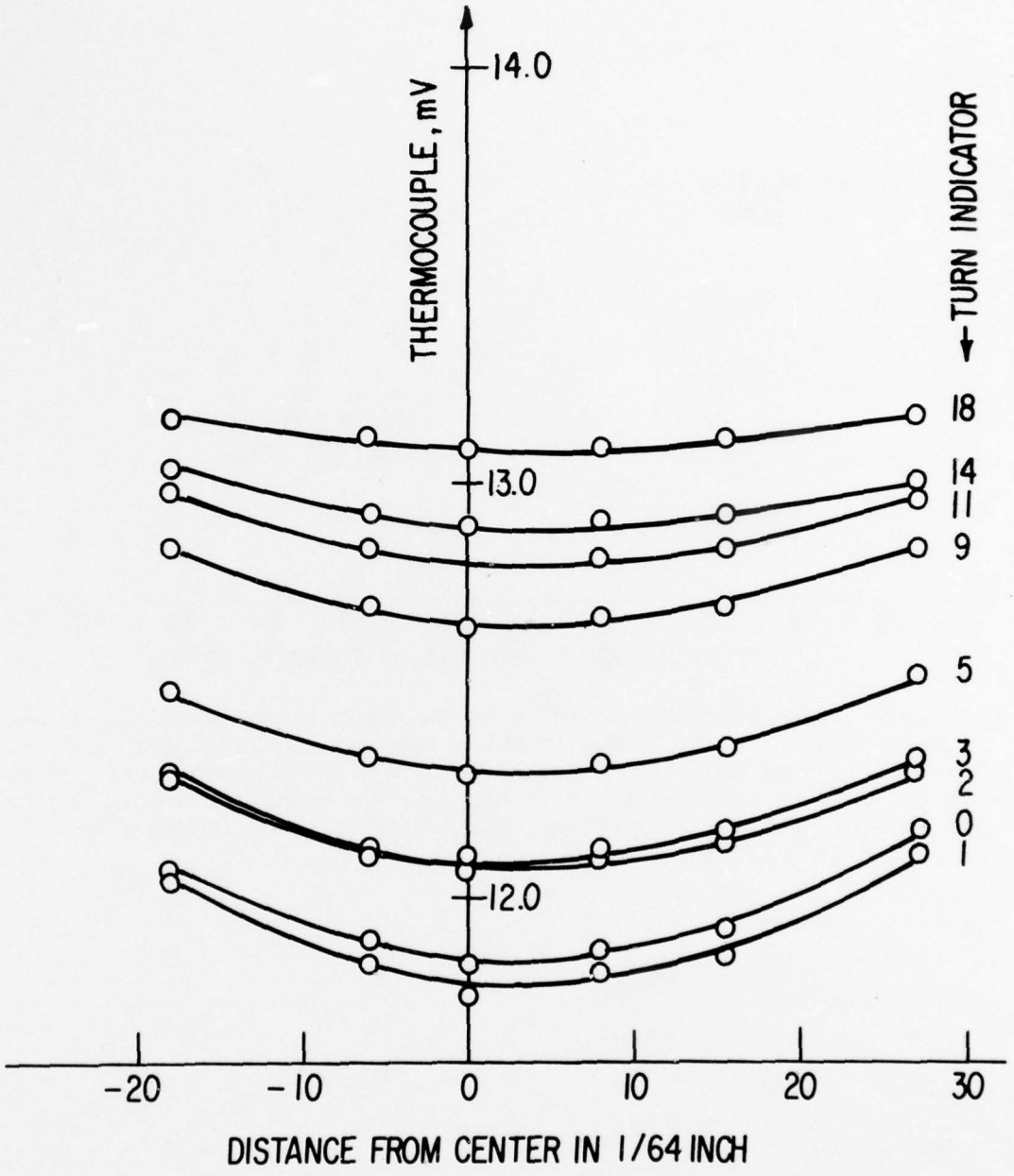

Figure A-5. Radial temperature distribution near the 5" position. The thermocouple gang is moved up from the "0" turn indicator position (which corresponds to 4.3" above the lower furnace port) to other turn indicator positions. One turn equals 1/16". The furnace core is filled with alumina powder. The upward curvature in the radial temperature distribution similar to those in Figure A-2 implies downward curvature in the isothermal contour similar to those in Figure A-3.

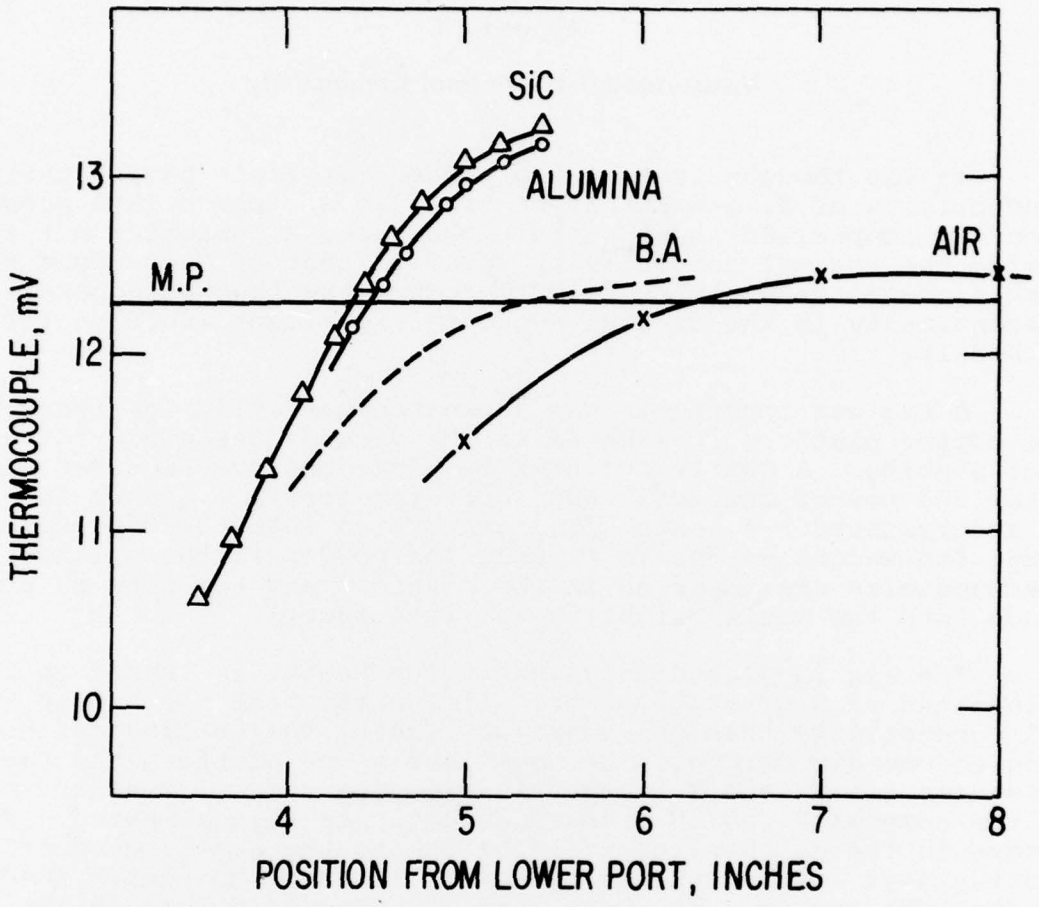

Figure A-6. Effect of the material in the furnace core on the thermal profile. Thermocouple reading of the center thermocouple in the gang used to obtain the radial profile Figure A-5 is plotted as a function of the vertical position when the gang container is filled with SiC, alumina, or air, at the same furnace power settings. The dashed line labeled B.A. is obtained with air core under baffled condition thus illustrating the effect of convection. With solid GaAs the similar curve would probably move further to the left. M.P. indicates the melting temperature millivolt equivalent for GaAs.

Appendix C

Measurement of Thermal Conductivity

It was thought that if two powder materials having thermal conductivity of K_1 and K_2 can be mixed in an appropriate proportion and compressed under certain pressure, a composite material having the thermal conductivity equal to that of GaAs could result. Such a composite would be used to reduce the thermal conductivity discontinuity in the crystal regrowth experiment (Section III B, Method 1).

A rig was constructed as shown schematically in Figure A–7. The copper platform is mounted to the vacuum base plate for good heat sinking. A quartz cylinder is placed on the recessed platform, and powder compact 0.490 inch diameter, 1.1 inches long can be accommodated. A heater is incorporated into the top copper plug; its weight serves to compact the powder in the cylinder. Thermocouples are inserted in the platform and top plug to protrude into the powder right at the interface.

The rig is placed in vacuum. The heater is turned on and maintained at a constant power. If the material has higher thermal conductivity than the quartz cylinder, the heating can be considered one-dimensional. At equilibrium the platform and cap temperatures are T_1 and T_2 respectively. The thermal conductivity of the composite having a known geometry is then computed. The errors in the calculation would be due to the quartz conduction, and the heat loss to the surroundings (vacuum and heater leads) by the heat source. The heat quantity conducted through the quartz can be subtracted from the input power if desired. With the high conductivity material of interest and with careful mounting, the errors are small.

To establish equilibrium, the thermocouple signals are fed to an x-y recorder. A typical trace is shown in Figure A–8 where the equilibrium is "indicated" by the time spent at a point. In this figure equilibrium is well approached at thermocouple readings T_1 = 0.28 mV and T_2 = 22.6 mV with 25 watts input. The thermal conductivity value from this curve is

$$K \leq \frac{25 \times 1.1 \times 4}{\pi \times 0.49 \times 2.56 \times (570-32)} \approx 5.2 \times 10^{-2} \text{ watts/cm } ^{\circ}\text{C}.$$

The powder used for this data was alumina, which in the compact form probably had smaller conductivity than the solid quartz cylinder, and hence the data is not very good. The 5.2×10^{-2} watts/cm $^{\circ}$C figure is slightly too high for quartz, if the samples were all quartz. The small temperature rise at the platform confirms the good heatsinking design. There is no way of knowing the amount of loss at the source, however, although at less than glowing temperatures the radiative heat loss in vacuum should be very small and the only other loss is through the electrical leads.

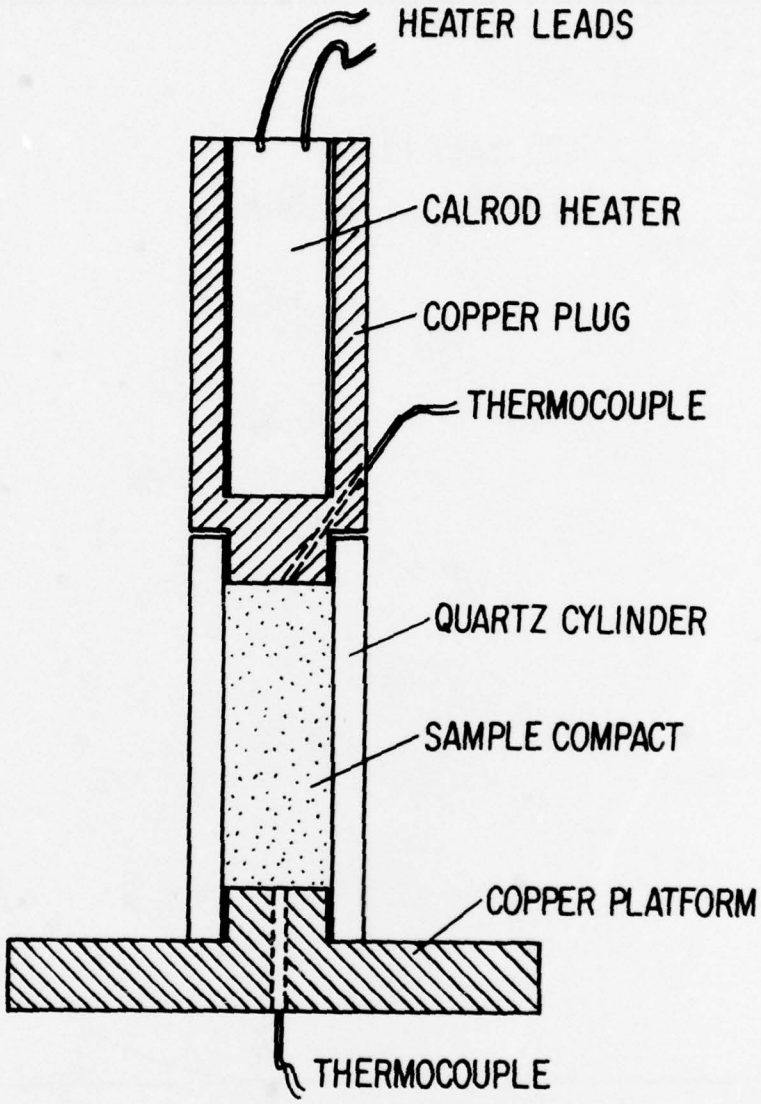

Figure A-7. Thermal conductivity measurement setup.

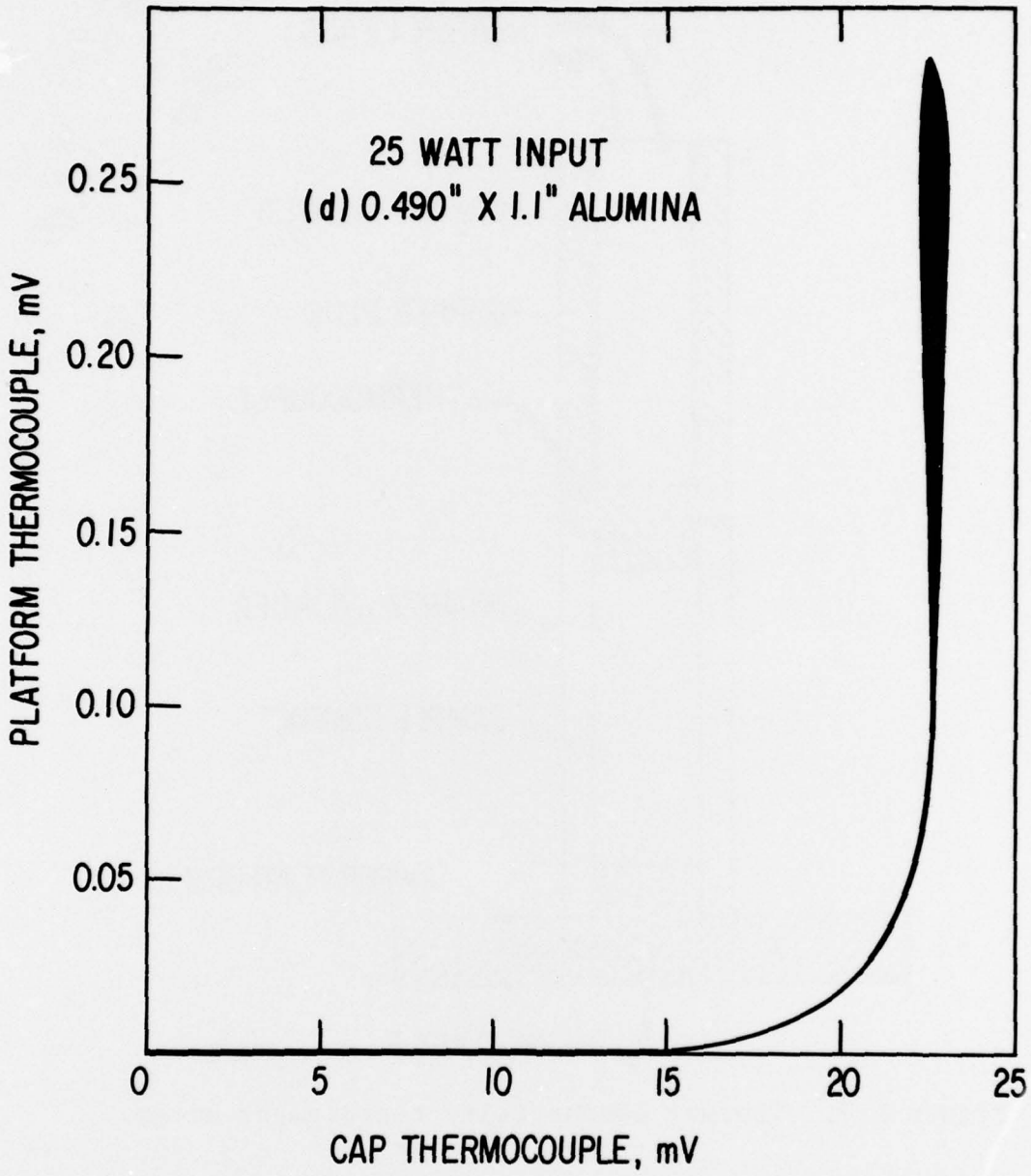

Figure A-8. Trace of the signal from the T_1 thermocouple vs that from T_2. The slowness of the change in temperatures is indicated by the thickness (caused by noises) of the trace.

Other compacts were also tried, such as SiC. As stated in the body of this report, Method 1 was not diligently pursued and the conductivity measurements were laid aside.